The Reversible Hydrides Solution for Hydrogen Storage

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Why $H_2$ for Transportation?

- Petroleum use heaviest in transportation sector
- Transportation emissions directly impact dense population centers
Hydrogen - A potentially clean and renewable energy carrier -

- High energy density
- Can be produced from renewable energy
- No pollution or CO₂ emissions from utilization
- Energy independent production

The Applications for hydrogen energy are here, But safe and practical Hydrogen Storage is not!

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Sandia’s Hydrogen Storage R&D Objective

Practical hydrogen storage for vehicle applications using reversible hydrides

Goals

• US-DOE Target: A hydrogen storage system with 6 wt.% H₂

• Improve performance: capacity, kinetics, thermodynamics, and cycle life

• Expand knowledge of hydrogen sorption phenomena in solid-state media
# Complex Aluminum Hydrides

High Gravimetric Hydrogen Capacities!

<table>
<thead>
<tr>
<th>Example</th>
<th>Capacity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(AlH$_4$)</td>
<td>5.6 wt%</td>
</tr>
<tr>
<td>Li(AlH$_4$)</td>
<td>7.9 wt%</td>
</tr>
<tr>
<td>Zr(AlH$_4$)$_2$</td>
<td>3.9 wt%</td>
</tr>
<tr>
<td>Mg(AlH$_4$)$_2$</td>
<td>7.0 wt%</td>
</tr>
</tbody>
</table>

* *Theoretical Reversible Capacities*
**Background: Sodium Alanate - NaAlH₄**

- Discovered: (Finholt & Schlesinger 1955)
- Direct Synthesis: THF, 140°C, 150 bar H₂ (Ashby1958, Clasen 1961)
- Principal Use: Chemical Reducing Agent
- Characterization: (Dymova, Zakharkin, Claudy, Wiberg...)

- NaAlH₄ Melts 182°C
- PCT Desorption Measurements
- 2-step Decomposition

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Hydrogen from Thermal Decomposition of Sodium Alanates

Total Theoretical Capacity = 5.6 wt% hydrogen

\[
\text{NaAlH}_4 \rightarrow \frac{1}{3}\text{Na}_3\text{AlH}_6 + \frac{2}{3}\text{Al} + \text{H}_2 \rightarrow \text{NaH} + \text{Al} + \frac{3}{2}\text{H}_2
\]

3.7 wt.%

1.9 wt.%
Breakthrough Discovery! Reversible Hydriding

Reversibility under moderate conditions w/o solvents

Opened up a new class of Hydrogen Storage Materials.

( Bogdanovic’ and Schwickardi, MH96 )

H₂ Re-absorption to form NaAlH₄

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Thermodynamics

\[ \Delta H (\text{NaAlH}_4) = -37 \text{ kJ/mol } H_2 \quad \Delta H (\text{Na}_3\text{AlH}_6) = -47 \text{ kJ/mol } H_2 \]
Comparison with other Hydrides

van't Hoff Diagram

- NaAlH₄ is a low temperature hydride
- Na₃AlH₆ is one of the few medium temperature hydrides

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Phase Transitions & Reaction Rates

- Determined rates of individual reactions
- Observed formation of metastable intermediate phase
- Determined rates of individual reactions

Decomposition of undoped NaAlH₄ on heating to 175°C

Anisotropic lattice expansion on heating

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Sandia’s Advanced Materials Development

New Methods of Synthesis and Doping

- **Generation I:**
  Ti/Zr-Alkoxide liquid Catalyst / NaAlH₄ dried from THF

- **Generation II:**
  TiCl₃ solid Catalyst / NaAlH₄ dried from THF.

- **Generation III-A:**
  Direct Synthesis - TiCl₃ Doping: NaAlH₄ Directly from NaH and Al.
  Purification in THF solvent no longer required!

- **Generation III-B:**
  Direct Synthesis and TiCl₃ Doping: NaAlH₄ from Na and Al.
  Reduces raw material cost!

- **Generation III-C:**
  Doping with other Ti-halide precursors: Improved Kinetics!

- **Generation III-D:**
  Indirect Doping Process: Expands options for using new dopants!
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**Improvements in H₂ Gas Delivery**

**Generation I:**
Ti/Zr-Alkoxide liquid Catalyst
NaAlH₄ dried from THF

**Generation II:**
TiCl₃ solid Catalyst
NaAlH₄ dried from THF

**Generation III:**
Direct Synthesis
NaAlH₄ prepared from NaH, Al and TiCl₃
No solvents

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RGA Impurities in Desorbed Hydrogen
Trade-off between Capacity & Kinetics

- Reversible Hydrogen Capacity decreases with TiCl₃ doping level
- Desorption (and Absorption) Kinetics increases with TiCl₃ doping level
- There is a trade-off between improved kinetics and capacity loss
Cause of the Drop in Capacity

XRD showed the formation of NaCl through the reaction:

\[ 3\text{NaAlH}_4 + \text{TiCl}_3 \Rightarrow \text{Ti} + 3\text{NaCl} + 3\text{Al} + 6\text{H}_2 \]
Arrhenius Kinetics Measurements
Isothermal Desorption Rates v.s. Temperature

NaAlH$_4$

Na$_3$AlH$_6$

Effect of Catalyst Loading on Reaction Rates

Rate = \( k \exp\left(\frac{-Q}{RT}\right) \)

- Activation Energy changes with introduction of Ti - Different Mechanism
- Activation Energy is independent of catalyst doping level
- Rates increase with catalyst content

Recent Developments: Indirect Doping Process

- TiCl₂ Pre-reacted with LiH
- Requires initial activation cycles
- Suggests solid-state diffusion / lattice substitution
Indirect Doping Process

- Rates comparable with direct doping of 2 mol% TiCl$_3$
- Activation energies are similar to direct doping
- Independent of precursor
Engineering Properties of Alanates
Test bed studies 70 grams alanate

- Exothermic hydriding reaction
- Thermal conductivity similar to other hydrides
  \[ \text{poor:} K_{th} = 2 \times 10^{-3} \text{ joule/sec-cm-K} \]
Studies of Material Safety Issues

Interaction of Alanates with Containment Vessel Materials

- Leaching observed in Aluminum materials due to 50% aluminum deficient composition
- Lead to Long-term cycling studies of interaction between Alanates and vessel materials

Optical micrographs 6061 Al coupon
Automated hydrogen cycling apparatus

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Conclusion

• 1 atm $H_2$ released at: NaAlH$_4$ (33 °C) and Na$_3$AlH$_6$ (110 °C)

• Reversible capacity approaching 4 - 5 wt.%

• Trade-off between improved kinetics and in capacity

• 4wt.% $H_2$: 90% Absorption < 1 hr and Desorption < 5 hrs at 125 °C

• Sorption properties independent of Ti-halide precursor

• Direct Synthesis: Enhanced kinetics, no gaseous contaminants, reduced cost and complexity

• Safety aspects of materials compatibility tested
Outlook

• Better understanding of reaction mechanisms is needed
  - Fundamental studies aid development of advanced materials

• Kinetics must be improved
  - Advanced catalysts and doping procedures

• Second reaction plateau pressure must be increased
  - Elemental substitution

• Effects of contamination must be investigated
  - Further investigations into capacity loss

• Reversibility in other LT complex hydrides must be demonstrated
  - Li-alanates, Mg-alanates

• Safety issues must be evaluated and addressed
  - Engineering design and materials modification
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Thank you!